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A DIFFERENTIAL THERMOMETER

By ALAN W. C. MENZIES

DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY

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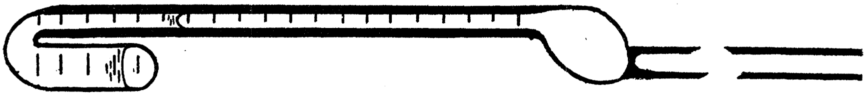
One type of differential thermometer measures the difference in temperature existing at the same location at different times; a second type measures the difference in temperature existing simultaneously at different points in space. The thermometer here described is of the latter type.



A well-known differential thermoscope of this type consists of two glass bulbs containing air, otherwise closed but communicating with each other through a U-tube partly filled with oil, whose change of level indicates change of temperature by responding to change of gas pressure within the bulbs. When this instrument is developed into a differential thermometer, certain disadvantages become apparent, of which three will here be mentioned. (1) If the manometric liquid is caused to run into one of the bulbs by accidental tilting, perhaps during transportation, then it is difficult to return the liquid into precisely the same position as it occupied when the instrument was scaled. If stopcocks are introduced in the effort to avoid this inconvenience, the cure may become worse than the disease, because of zero-creep. (2) In the presence of permanent gas, the manometric liquid becomes, in practice, not infrequently broken into threads, separated by short columns of the gas. (3) Although oils furnish very sensitive manometric liquids, their use, or, indeed, the use of any liquid other than the insensitive mercury, allows the entrance of an error that has been too little appreciated. The incidence of this error in tensimetric work has been pointed out by the writer in another connection.[1] The error in question is caused by the fact that a gas at higher pressure has a larger weight solubility than the same gas at a lower pressure. The permanent gas, always slightly soluble in manometric liquids other than mercury, therefore passes by a process of solution and diffusion from the side of higher to that of lower pressure. For this reason even stopcock-free instruments of the kind referred to suffer from slow zero-creep.

In order to avoid these and other disadvantages, all that is necessary is to abandon entirely the use of permanent gas. One selects as manometric fluid not oil but some liquid whose change of vapor pressure per degree in the range of temperature where the differential measurements are to be made is such as to cause differences of vapor pressure in the two bulbs of the thermometer that will register themselves by adequate differences of level in the manometer. The diagram, figure 1, shows one simple form useful in ebullioscopy, made from glass tubing a few mm. in bore and having, without its handle, a length of perhaps 12 cm. Permanent gas is removed prior to sealing by the process of boiling out familiar to many who have had occasion to measure vapor pressures. For reading the difference of level of the two liquid surfaces, a mm. scale may be etched on both limbs. For many purposes, water is a suitable filling liquid; but it is obvious that the sensitiveness in any particular range of temperature may be given widely different values according to the rate of change of vapor pressure and the density of the liquid selected. The change of temperature between upper and lower bulbs that will cause a change of level of, say, 1 mm. in the height of the column of the filling liquid may be computed in an obvious manner from the known vapor pressures and densities of this liquid, and the results tabulated with temperature as argument. Thus, for water, at 57°, 80°, and 100°, these values are 0.01180°, 0.004969°, and 0.002599°, respectively.

Although the thermometers are of different general types, as indicated above, it is perhaps of interest to compare this differential thermometer with the Cavendish-Walferdin[2] metastatic type as elaborated by Beckmann,[3] and as applied in the same field, for example that of ebullioscopy. With regard to length of scale per degree, the Beckmann mercurial type is limited by the usable size of bulb, and by the permissible narrowness of the capillary, so that a centrigrade degree corresponds customarily to 40 or 50 mm. movement of the mercurial thread. The type here described is not thus limited in this respect, for a very low-boiling liquid may be used for filling. With the simple water filling, however, one degree centigrade at 80°, a temperature close to the boiling-points of the two favorite solvents benzene and ethyl alcohol, corresponds to an observed change of length of over 200 mm. In both types the length of degree varies with the actual temperature. As to range, the Beckmann type is restricted to that between $-39°$ and $+250°$ C.[4] While this is a much larger range than can be conveniently covered by the use of a single chosen liquid in the newer type, the simplicity of construction makes possible such a wide choice of filling liquids that a much wider range is easily available in the direction of lower as well as of higher temperatures. In comparing precision, one has to bear in mind, for the Beckmann type, possibilities of error due to (1) lack of uniformity of bore, (2) hysteresis in change of volume of bulb, (3) effect of pressure on volume of bulb, (4) sticking of mercury in capillary, (5) exposed thread, (6) difference of radiation to and from bulb, (7) departure of apparent degree from true degree. For the type here described, no one of the first six of these sources of error is important, for reasons that will be sufficiently obvious. In regard to (6), it may perhaps be said that the change with environment of radiation loss suffered by a Beckmann thermometer at temperatures far from room temperature is here largely eliminated because suffered alike by upper and lower bulb. With regard to (7), it is indeed most necessary to employ a factor, different for each temperature, to convert observed readings to temperature; and this factor may be criticized as inconvenient to use, inaccurate in value and laborious of computation. But the use of a similar factor is likewise necessary, albeit frequently neglected, in the case of the Beckmann thermometer, whose degree, if true at 0°, is, for example, about 3% in error at 80°.[5] The accuracy of the conversion factor for the newer type is dependent in part on the accuracy with which the vapor pressure of the filling liquid is known. For such liquids as would be employed, and within the ranges of temperature that come here in question, this quantity, the vapor pressure, can now be measured to better than one part in one thousand.[6] The table that will be published for the filling liquid water, in a more comprehensive article elsewhere, was derived by differentiation from the highly satisfactory, if cumbrous, equation connecting temperature and vapor pressure of water given in the 1918 edition of the Smithsonian Meteorological Tables, and has an accuracy of just this order. The process of computing factors for, perhaps, each tenth part of a degree over a considerable range of temperature may indeed be laborious; but, once published, the factor table may be used by everyone. This inconvenience, therefore, is shifted from the shoulders of the user of the thermometer to those of him who first computed the table. It may be added that the Beckmann type is considerably more cumbrous as well as very much more fragile than the type here described, which one constructs from stout-walled Pyrex tubing.

In certain respects, therefore, it would appear that this type of differential thermometer has advantages over the Walferdin metastatic type as elaborated by Beckmann; and the question arises as to whether such other factors as are peculiar to a given application are favorable to its use. In studying its application in ebullioscopy, for example, as outlined in the article following, one finds that the important disturbing factor, peculiar to ebullioscopy in its incidence, of barometric fluctuation does not measurably affect the readings of the newer type, while such pressure fluctuations are one of the chief outstanding sources of error when the metastatic type is used. Another application in a different field may be described in the near future.

[1] Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **42**, 1920 (1951–1956).

[2] Cavendish, *London, Phil. Trans. Roy. Soc.*, **50**, 1757 (300); Walferdin, M., *Bull. Soc. geol. de France*, **13**, 1841–2 (113).

[3] Beckmann, E., *Leipzig, Zeit. physik. Chem.*, **2**, 1888 (644); **51**, 1905 (329).

[4] Cf. Staehler, A., *Leipzig, Arbeitsmethoden in der Anorg. Chemie*, **3**, i, 1913 (106).

[5] Staehler, A., *Ibid.*, p. 108.

[6] Cf. Smith, A., and Menzies, A. W. C., *Easton, Pa., J. Amer. Chem. Soc.*, **32**, 1910 (1412–1434).